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HIGH-POROSITY CELLULAR MATERIALS
BASED ON ALKALI ALUMINOBOROSILICATE GLASS

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A method for obtaining high-porosity cellular material based on alkali aluminoborosilicate glass by the consumable additive method is examined. One form of this method is to burn out a polymer matrix (polyurethane foam). The effect of the structural parameters and properties of the glass on the process of obtaining high-porosity blanks and the dependence of the strength characteristics on the porosity of the samples and the specific surface area of the glass powder are studied.

The glassy state of matter opens up extensive technological possibilities for obtaining diverse materials and articles.

The increasing number studies in organic and inorganic catalysis, membrane technology, and biochemistry has generated great interest in porous glasses. The distinguishing features are springiness, wide pore-size range, and a reactive surface.

Among macroporous materials, high-porosity cellular materials (HPCMs) based on various types of ceramics and metals are winning increasing popularity. Such materials are used for filtering hot air flows and molten metals, for manufacturing catalyst carriers and heat-shielding elements, in mass transfer processes, and in other applications. Such materials are characterized by an extended specific surface and low apparent density [1]. The production of HPCMs is based on the principle of depositing a layer of matter (metals, oxides, carbides, and other substances) on the surface of an organic structure-forming matrix and then sintering this layer and removing the matrix by thermal destruction. Polyurethane foam is used as the organic structure-forming matrix. Structurally, this foam consists of a three-dimensional framework consisting of bridges whose transverse cross section is a curvilinear triangle [2].

An important feature of such materials is a high-temperature sintering range, reaching 1500 – 2000°C. In this connection, they are capable of withstanding high temperatures under working conditions without failure. However, there are technological processes where the working conditions are less stringent and high temperatures are not required. The problem of developing a glass-based high-porosity material

for low-temperature chemical processes and decreasing the production costs by using raw materials which are cheaper than the traditional ceramics was posed at the D. I. Mendeleev Russian Chemical Engineering University. In this case, the temperature range for using glass-based materials decreases to 650 – 720°C depending on the composition of the glass.

Since one of the main requirements for obtaining HPCMs is resistance to chemical attack, a decision was made to use the alkali aluminoborosilicate system. This system is used in chemical laboratories, which presupposes resistance to water and acid solutions. The unified aluminoborosilicon-oxygen framework will impart the desired strength to the glass and, in consequence, to the high-porosity material.

It is well known that the boron ions in borosilicate glasses can occupy trigonal and tetrahedral positions. Two factors determine the amount of boric anhydride that transforms into tetrahedra — the amount of oxygen which metal oxides bring to the glass and the silica content of the glass. The oxygen number (OXN) is used as a quantitative characteristic of the relative amount of the total oxygen that remains per boric anhydride unit. The numerical value of this number for each specific glass can be calculated from the formula

$$OXN = (R_2O - Al_2O_3)/B_2O_3,$$

where R_2O is the molar content of the alkali oxides in the glass.

The alkali aluminoborosilicate system must contain a sufficient alkali metal for each boron atom to have four-fold coordination so that acid solutions cannot wash out the alkali borate component. An example is the well-known fact that

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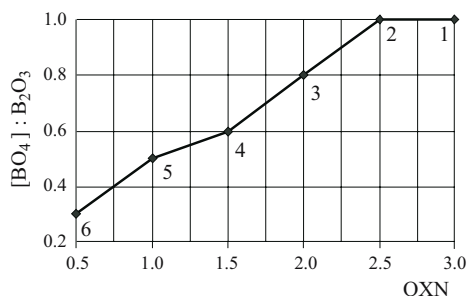[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

Fig. 1. Relative content of tetrahedral boric anhydride as a function of the oxygen number: *1 – 6*) experimental compositions.
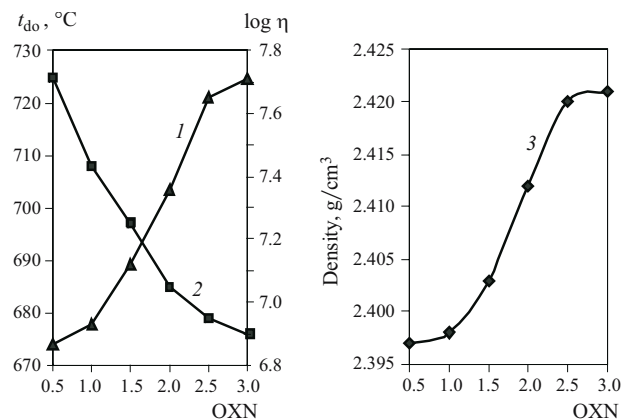

Fig. 2. Low-temperature viscosity (*1*) at the deformation onset temperature (*2*) and density (*3*) versus the oxygen number.
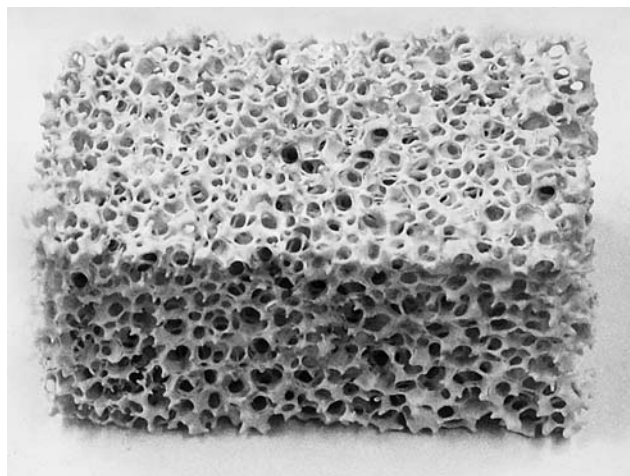

Fig. 3. High-porosity cellular material.

there exist microporous alkali borosilicate glasses whose compositions are characterized by a low ratio $Na_2O : B_2O_3$, which ordinarily does not exceed 1/3. Boron with three-fold coordination is a chemically unstable integral component, and acids can easily wash it out of glass acids together with the sodium oxide with which it is bound. To prevent this, a certain excess of the alkali component is introduced so that all of the boron would have four-fold coordination. Then, the boron ions penetrate into the silica framework and replace the silicon ions in it, i.e., the integral borate component gradually vanishes and forms a single silicon-boron-oxygen framework.

A small quantity of Al_2O_3 was added to suppress liquation in the glass [3]. The simultaneous presence of aluminum and boron in glasses together with excess alkali-metal oxides results in the formation of a unified aluminoboron-oxygen framework. When Al_2O_3 is introduced into the glass, the density, modulus of elasticity, and hardness all increase. In our case the CLTE increases from 84×10^{-7} to $92 \times 10^{-7} K^{-1}$ when Al_2O_3 is substituted for some of the SiO_2.

According to Sobolev's rule, a transition to a higher OXN compacts the ion packing, which saves space, and decreases the specific volume, as a result of which the density, refractive index, hardness, and strength and chemical stability of the crystal lattice all increase. The experimental data and structural studies show that the doctrine about coordination and mutual interchangeability of the ions in crystalline silicates can be transferred in general form, but with certain distinctive features, to the glassy state of silicates also [4].

A series of glasses (six compositions) with the aluminum oxide content increasing and the silicon oxide content decreasing was synthesized. Analytically pure grade and pure grade reagents were used to make the batch. The ready batch was mixed to a uniform state. Glass was made in a gas furnace at temperatures 1500 – 1570°C.

The content of [BO_4] tetrahedra in the overall content of B_2O_3 in these glasses was determined and a plot versus the OXN was constructed for each concrete composition (Fig. 1). The data obtained were correlated to the results of IR spectroscopy — the absorption bands of the glasses in the region $1000 – 1250 cm^{-1}$ characteristic for [BO_4] and the absorption bands in the region $700 – 800 cm^{-1}$ characteristic

for [AlO_4] were traced. Absorption bands at $1350 – 1450 cm^{-1}$, attesting to the transition of boric anhydride into the trigonal form, first appeared in the spectrograms for the No.3 glass composition. Since the transition of boron from three- to four-fold coordination became apparent in the analysis of the structurally sensitive properties of the glasses, the OXN as a function of the deformation onset temperature, density, and low-temperature viscosity of all six compositions was investigated (Fig. 2).

Evidently, the OXN, and in particular the presence of trigonal or tetrahedral boric anhydride itself, affects the deformation onset temperature, the viscosity, and the density of the glass. This is seen especially clearly in the curves of the viscosity and density, where a kink is observed at OXN close to 2.5. This is explained by the structural transformations occurring in the glass.

In summary, the differing coordination state of boron ions in aluminoborosilicate glasses affects the physical – chemical properties of the glass. This must be taken into account when articles as complex as HPCMs are manufactured.
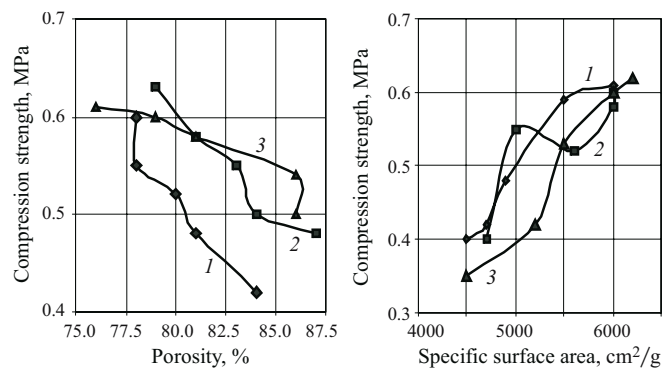
Fig. 4. Compression strength versus porosity of the samples and the specific surface area of the glass. The numbers of the curves correspond to the composition numbers.

The consumable additive method was used to create a porous structure. High-porosity samples were obtained by depositing a layer of material (glass powder) on the surface of an organic structure-forming matrix consisting of polyurethane foam and then sintering the layer and removing the matrix by thermal destruction [5].

The slip suspension method with water glass as the dispersion medium was used to deposit the glass powder on the polyurethane foam. The size of the glass powder particles was $5 – 6 \, \mu m$, which corresponds to specific surface area $4.5 – 6.2 \, m^2/g$. The samples underwent heat-treatment in a Silit furnace. The final heat-treatment temperature was varied according to the composition of the glass.

High-porosity cellular samples with average cell diameter $2 – 4 \, \mu m$ and porosity $82 – 88\%$, depending on the structure of the initial polyurethane foam, were obtained (Fig. 3). According to their water resistance the glasses belong to the second hydrolytic class (mass losses $0.11 – 0.2 \, mg/g$).

The strength characteristics of the samples were also studied as a function of the porosity and specific surface area of the glass powder. The values of the first three glass compositions are presented as an example in Fig. 4.

In summary, it can be concluded that further studies of the physical – chemical properties and structure of high-porosity cellular materials made of glass belonging to the alkali aluminoborosilicate system are needed in order to use these glasses in chemical processes where extended surface area, high macroporosity, chemical stability, and mechanical strength are important.

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